

A Comparison of Four Commercially Available Portable Raman Spectrometers

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Abstract

The objective of this presentation is to discuss the results of the evaluation studies conducted on four commercially available field-portable Raman spectrometers. The data presented in this comparison will affect the forensic science community by assisting a prospective user in determining which portable Raman device may best suit their agency's needs. This presentation describes:

- The specifications of the four portable Raman instruments as evaluated in this study.
- A summary of the results and discussion of the technical evaluations.
- The strengths and opportunities for improvement of each device as perceived by the evaluators.
- A discussion of the limitations of portable Raman technology regarding the analyses of controlled substances and explosives performed in these evaluations.

Introduction

There are numerous and varied portable Raman spectrometers currently available for purchase. These rugged, field-portable units are specifically designed to provide law enforcement, airport security, border patrol, military, emergency service personnel and other first responders with the ability to perform non-destructive analyses on unknown bulk powders and liquids containing compounds such as illicit and pharmaceutical drugs, explosives, ignitable liquids, oxidizers, industrial chemicals and common household materials. Evaluation of these portable Raman spectroscopy instruments is critical to the advancement of forensic science, homeland security efforts and military operations. These devices hold the promise of empowering first responders with crucial forensic intelligence, enabling them to make the best decisions to preserve public safety. They have further potential to help reduce the burden on overtaxed crime laboratories, by effectively screening out and prioritizing evidence before forwarding it to the forensic laboratory for additional testing.

The National Forensic Science Technology Center (NFSTC), as part of its Forensic Technologies Center of Excellence (FTCoE) award from the National Institute of Justice (NIJ), evaluated four portable Raman spectrometers. The instruments evaluated were the ICx Technologies Fido® Verdict™, the DeltaNu® ReporteR™, the Thermo Scientific® FirstDefender RM™ and the Smiths Detection RespondeR™ RCI. These technical evaluations were conducted to provide potential users of this type of portable Raman technology with independent and unbiased technical information on each of these devices.

Methods and Materials

Each spectrometer was tested separately using the same standardized, systematic evaluation scheme to assess individual strengths, areas for improvement, limitations, graphical user interfaces and safety issues, as well as the entire chemical characterization process involved from sample introduction through result output for each device. Representative samples of controlled and non-controlled drugs (standards and adjudicated case samples), drug diluents, ignitable liquids, explosives, explosive precursors and common household and laboratory compounds were used to assess each unit for conformity, mixture sensitivity, specificity, portability and ruggedness. Samples were added to disposable glass vials, analyzed in triplicate, and the resulting data and evaluator observations were recorded. Accuracy and reproducibility were examined for each set of data and were defined in the individual technical evaluations. Data for the FirstDefender RM and RespondeR RCI reflect samples analyzed using the internal sampling method (“vial mode”)*, while data for the Verdict and ReporteR reflect data analyzed using the external sampling method (“point-and-shoot mode”). **Ruggedness for the FirstDefender RM was measured with the point-and-shoot mode.*

For the full technical evaluation of each instrument please visit the NFSTC website at: <http://www.nfstc.org/lab/technology-evaluations>

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Conformity Trials:

The following 25 compounds and mixtures were used to determine the instruments' abilities to accurately identify known compounds of interest: cocaine HCl, cocaine base, methamphetamine, heroin, mannitol, niacinamide, boric acid, inositol, caffeine, quinine, RDX, ammonium nitrate (prills), ammonium nitrate (powder), ammonium perchlorate, sugar, cumin, urea nitrate, mineral spirits, BP® 87 octane gasoline, BP diesel fuel, kerosene, Klean-Strip® VM & P Naptha thinner, Lamplight® lamp oil, Ronsonol lighter fuel®, and Kingsford® charcoal lighter fluid.

Mixture Trials:

Four controlled substances mixture series and two explosive mixture series were analyzed in triplicate in order to determine the instruments' mixture series abilities to detect components in a mixture. Five mixture ratios were prepared by weight of the target compound to the weight of the diluent as follows: 80:20, 60:40, 50:50, 40:60, and 30:70. Cocaine HCl and cocaine base were mixed with caffeine; heroin was mixed with quinine; methamphetamine was mixed with dimethyl sulfone; and ammonium nitrate was mixed with sugar in one series and with cumin in another series.

Specificity Trials:

The following 28 compounds and mixtures were used to determine the ability of each instrument to differentiate between compounds similar in structure or function to target compounds and/or those commonly associated with target compounds, such as controlled substance cutting agents: d,l- amphetamine sulfate, MDMA (3,4-methylenedioxymethamphetamine), MDA (3,4-methylenedioxyamphetamine), MDEA (3,4-methylenedioxyethylamphetamine), morphine sulfate, codeine sulfate, benzocaine, lidocaine, procaine, acetylsalicylic acid, ibuprofen, guaifenesin, diphenhydramine, chlorpheniramine, pseudoephedrine, dimethyl sulfone, baking soda, acetaminophen, urea, ferric nitrate, sodium perborate, fertilizer (13% total nitrogen) prills, fertilizer (13% total nitrogen) ground,

turmeric:cardamom mixture (50:50), sodium hydroxide (lye), sulfuric acid, ammonium hydroxide, and citric acid.

Portability Trials:

The instruments were transported to the Manatee County Sheriff's Office to test a variety of adjudicated controlled substance case samples in the Chemistry Laboratory. Each sample was tested by three evaluators. A performance check was performed by each evaluator before proceeding. Samples included six tablets, seven cocaine HCl and base exhibits, five heroin exhibits, and two exhibits in which no controlled substance was detected (lidocaine, and presumably acetaminophen). Tablets were crushed and transferred into appropriate containers (culture tubes or vials) before testing. Since certain tested pharmaceutical tablets have such a large percentage of acetaminophen, and this substance could help identify a tablet, the identification of acetaminophen was defined as a positive for these tablets. One sample's identity (presumed to be acetaminophen only) had not been reported by the Sheriff's Office (reported as "no controlled substances identified"). Results from analyzing this sample were used only for reproducibility.

Results

The accuracy and reproducibility results of each set of data are listed as percentages in the following charts (Chart 1 and Chart 2) as percentages. The requirements for accurate and reproducible results for each instrument are briefly outlined, and the full data sets are available in the individual evaluations (listed in "References").

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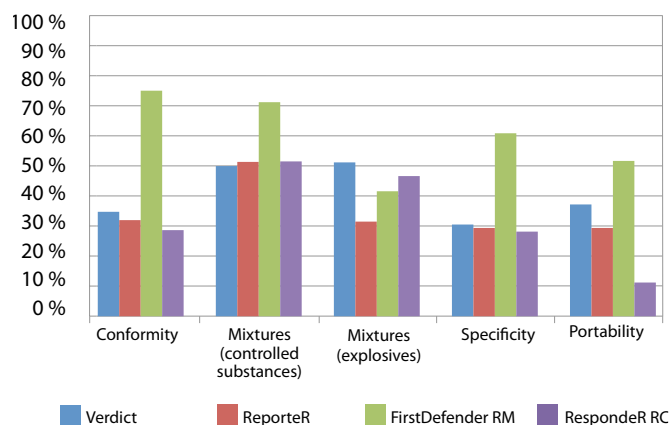
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Accuracy

Criteria for Accuracy	
Verdict	The sample was the most-correlated result (or synonym) or one of multiple equally most-correlated results. For mixtures, either of the components was the most-correlated result or one of multiple equally most-correlated results.
ReporteR	The sample was the most-correlated result (or synonym) or one of two equally most-correlated results. For mixtures, either of the components was the most-correlated result or one of multiple equally most-correlated results.
FirstDefender RM	The sample was a match (or synonym), or one of the compounds listed in a mixture.
ResponseR RCI	The sample was the most-correlated result (or synonym) or the residual search result from the most-correlated result.

Chart 1: Percentage (%) Accuracy by Sample Set



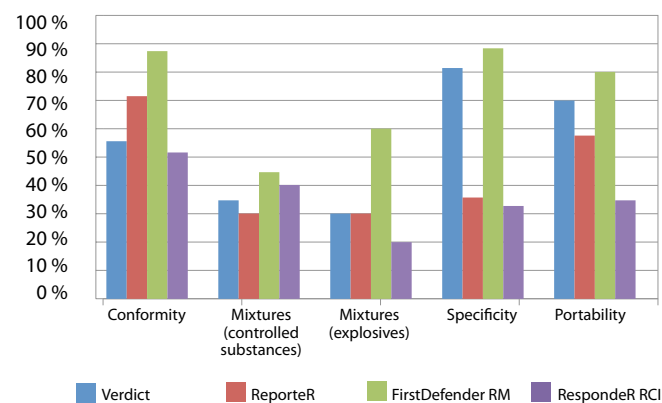
Discussion

The FirstDefender RM demonstrated the highest degree of accuracy in all but the explosive mixture sample set, in which the Verdict and ResponseR RCI performed more accurately. The FirstDefender RM results may have been partly due to the additional “mixture” category of results. The other instruments performed similarly to each other, with the exception of the ResponseR RCI, which had poor accuracy in the portability sample set. The accuracy for all instruments in the portability set, which was made up of casework samples, was near or below 50%.

Reproducibility

Criteria for Reproducibility	
Verdict	The most-correlated or equally most-correlated result matched for all three replicates. Includes results that were all “no match”, incorrect matches, and synonyms.
ReporteR	The most-correlated or equally most-correlated result matched for all three replicates. All must also be “matches” or all “no matches”. (All “no match” results were given equal correlation value.) Includes results that were “no match”, incorrect matches, and synonyms.
FirstDefender RM	The “match” result, one of multiple “match” results, and/or the first listed match result in a mixture (mixture result with the highest percentage) were the same for all three replicates. Includes results that were “no matches found”, synonyms, “no match” results, incorrect results and, “excessive analysis time” results. Does not include “similar” results, unless all three trials produced the same “similar” result.
ResponseR RCI	The result with the highest hit quality matched for all three replicates. Includes “no match” results, incorrect results and synonyms.

Chart 2: Percentage (%) Reproducibility by Sample Set



Discussion

Overall, the FirstDefender RM performed with the most reproducibility between trials, followed by the Verdict, ReporteR and ResponseR RCI, in that order. However, a potential buyer should factor in the requirements for reproducibility used in this chart. For example, three negative or three incorrect results for an instrument were still considered reproducible, while correct, but different results (e.g., cocaine and caffeine) across trials were not considered reproducible. The mixture feature, available only on the FirstDefender RM, allowed for single match results and matches across the trials in a mixture sample to be counted as reproducible.

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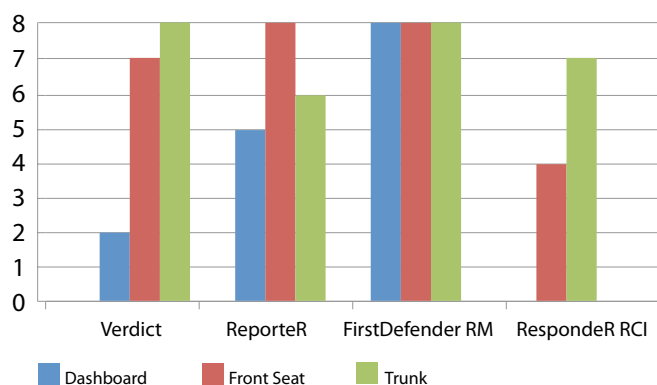
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Ruggedness Trials

Chart 3: Number of Accurate Results per Trial per Instrument



A representative group of eight compounds was selected for ruggedness testing after each instrument was subjected to the heat stressors of the dashboard, front seat, and trunk of a car. These trials were intended to model some of the storage and transportation practices by law enforcement officers, first responders, and field users. After each two-hour trial, the temperature was recorded, the instrument was performance-checked, and the eight-compound sample set was analyzed.

Discussion

The Verdict, ReporteR, and FirstDefender RM performed similarly to laboratory conditions despite being subjected to temperatures at or above the recommended storage and usage temperatures. The ReporteR returned six of eight correct answers despite failing the performance check prior to sampling. The Verdict struggled with the hottest trial on the dashboard, returning only two correct responses. The RespondeR RCI required service after one of the dashboard trials and repeatedly failed the calibration check after a second dashboard trial.

Discussion of Evaluation:

Statements in “Strengths” and “Areas for Improvement” are based on the evaluations performed^{1,2,3,4} at NFSTC and the perceptions of the evaluators.

Strengths

- Testing is non-destructive and can be accomplished through sample vials, ensuring the integrity of the evidence.
- All of the evaluated units are easy to operate.
- Analysis time on the Verdict and ReporteR is very short.
- Very little sample preparations is required prior to analysis
- The Verdict, ReporteR, and RespondeR RCI return results with correlation (or hit-quality) scores to aid the user in interpretation of results. The FirstDefender RM lists multiple results and, for mixture results, lists the percentage match for each result.
- After exiting the result screen, it is possible to view results on the instrument on the FirstDefender RM, RespondeR RCI, and ReporteR. The RespondeR RCI enables the user to label each scan by incident and file name.
- The FirstDefender RM reports matches, similar spectra, mixtures, and multiple matches.
- The RespondeR RCI can be linked to other Smiths Detection instrumentation using additional software for infrared chemical analysis (not tested).
- Comparison software is directly built into the FirstDefender RM and the RespondeR RCI.
- The RespondeR RCI is equipped with an internal calibration standard, and sampling can only continue if the instrument passes the check or calibration, if necessary.
- All instruments are equipped with safety features to remind users of potential injury from laser energy.
- User library additions are possible in the ReporteR, FirstDefender RM, and the RespondeR RCI.
- The methods on the FirstDefender RM and RespondeR RCI can be edited to tailor the sampling for the user in areas such as sampling time, laser strength, or libraries for comparison.

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Areas for Improvement

- Ignitable liquids are inaccurately identified in the majority of trials. Instead of the identification of a brand name product, a more general library entry, such as “petroleum product” may be more accurate and/or useful to the user.
- The inclusion of more phenethylamines in the libraries may produce more accurate results and target an ongoing controlled substance problem.
- Retrieving data for later review is increasingly important. On each instrument, the file is given an identifier, but on the ReporteR and Verdict, this is unknown to the user unless he/she keeps a careful log, by date of each sample analyzed. The display and/or the ability to name a sample with a unique identifier would assist the users and technical reviewers in retrieving and reviewing data.
- Mixture deconvolution is not possible on the ReporteR or Verdict. The residual search function on the RespondeR RCI returned few accurate results during the evaluation. Mixture reporting on the FirstDefender RM can be somewhat misleading.
- Reporting data from the instruments requires transfer of files to another computer. Having the ability to print a report directly from the instrument would increase the ease of use.
- Sampling on the RespondeR RCI takes a considerable amount of time and user attention.
- The RespondeR RCI requires a 15–30 minute warm-up period before the calibration check can pass.
- Though technically portable, the RespondeR RCI is the heaviest of those evaluated and is not a hand-held instrument. This specification limits its use in the field.

Limitations of Raman Spectrometry

- Portable Raman spectroscopy does not work well with trace evidence. A sufficient quantity of the compound of interest must be available for sampling.
- Raman spectroscopy does not work well on highly fluorescent or pigmented items.
- Raman scattering is an inherently weak signal that can be affected by background light, leading to spectra of poor quality.
- The identification of materials is generally limited by the reference samples contained in the library and/or those added to the user libraries.
- The identification of a compound in a mixture does not necessarily correspond with the compound in the highest ratio in the mixture.
- Proper training must be conducted in order to correctly interpret results.
- The use of Raman spectroscopy is not inherently safe. Both eye hazards and explosion hazards exist if the unit is used incorrectly.
- Raman scattering is limited to molecules that have a change in polarization potential in regard to distance between nuclei.
- Though Raman spectroscopy is considered a confirmatory test, emphasis on spectral comparison in training is important. All the instruments evaluated for this study returned results of their search algorithms that were inaccurate. The ability to confirm a chemical depends on many factors including (but not limited to):
 - » The purity of the chemical being tested
 - » The presence of the chemical in a library
 - » The search algorithm of the instrument
 - » The background interference
 - » The color of the chemical
 - » The fluorescence of the chemical
 - » The Raman scattering activity of the chemical
 - » The particles of a sample in the focus of the Raman laser
 - » The limited focal area of the laser

Instrumentation Specifications*



ICx Fido® Technologies Verdict™,
Model #FV-01-A
Serial #07000113A
Serial # 07000113



DeltaNu® ReporteR™
Model #2.11
Serial #701-009



Thermo Scientific® FirstDefender RM™
Software 3.3.0
Serial # RM2245



Smiths Detection Responder™ RCI
Model #024-1001
Serial #502601108E, and 501511106A

	ICx Fido Verdict (point-and-shoot mode)	DeltaNu ReporteR (point-and-shoot mode)	Thermo Scientific FirstDefender RM (vial mode)	Smiths Detection Responder RCI (vial mode)
Price	\$17,485 MSRP, \$15,982 GSA	\$15,000 USLP plus shipping	~\$50,000 MSRP, \$48,500 GSA	\$30,000 (+for library upgrades) \$2,625 communication upgrade (Bluetooth®)
Price includes	<ul style="list-style-type: none"> • Hardware • Standard and right angle sampling heads • Polystyrene reference standard • Laser safety goggles with lens cloth • micro SD card • Hex Key 0.050 • USB cable • Enabler™ Software CD • Operator's Manual • USB Wall Charger 	<ul style="list-style-type: none"> • Hardware • Three sampling tips • Polystyrene reference standard • Laser safety goggles • NuSpec™ Software • Chargers • USB cable • Libraries • 250 sample vials 	<ul style="list-style-type: none"> • Hardware • Pelican case • Polystyrene standard • Chargers • Rechargeable 3.7V lithium ion battery and disposable OTS Surefire® batteries • Lithium battery charger • Power supply cord with multiple plug adapters • A memory card and reader • Sample vials 	<ul style="list-style-type: none"> • Hardware • Pelican case • (Internal standard) • Laser safety goggles • Sealed data compartment including power port • Battery Charger • USB storage device • Flexible keyboard(USB) • 1 year Standard Warranty • Regional training class for up to 3 people • 100 sample vials, spatula and pipettes
Size (L x D x W)	19 cm x 4.1 cm x 8.6 cm (7½" x 1⅝" x 3⅜") (includes external sampling tip)	13 cm x 3.8 cm x 6.3 cm 5.25" x 1.5" x 2.5"	19 cm x 4 cm x 11 cm 7.6" x 1.75" x 4.2" (includes external sampling tip)	22 cm x 9.9 cm x 19 cm 8.75" x 3.88" x 7.5" (does not include external sampling port)
Weight	430 g (0.95 lb)	397 g (0.88 lb)	816 grams (~1.8 lbs)	3.1 kg (6.9 lbs)
Library size	Not listed	~315 (standard law enforcement)	~8,550	~9,400
Sampling Method	External	External	External & Internal	External & Internal
Software	Enabler (external)	NuSpec (external)	Internal	Internal
Data format	dnu (in evaluation); .spc, .prn (listed in manual)	.dnu, .spc, .prn	.jpg, .spc, .txt, .arb, .lrd	.rar
File Identification	Chronological	Chronological	Chronological by "session" (user-named); results list numerical identifier	Incident, file name, comments
On-instrument data review	No	Yes, by date	Yes, by session	Yes, by incident and file name
Spectral resolution	12 cm ⁻¹	~ 12 to 15 cm ⁻¹	7 to 10.5 cm ⁻¹	12 cm ⁻¹
Spectral range	300 to 2000 cm ⁻¹	300 to 2000 cm ⁻¹	250 to 2875 cm ⁻¹	225 to 2400 cm ⁻¹
Operating temp. range	-20 to 40°C	-20 to 40°C	-20 to 40°C	7 to 50°C
Storage temp. range	not listed	-30 to 60°C	-30 to 60°C	-20 to 80°C

* As of evaluation preparation

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Conclusion

The choice of purchase of a portable Raman spectrometer is dependent on the specific needs of the agency. These may include features such as the ability to print reports, compare spectra on the instrument, or withstand extremes in climate. While the FirstDefender RM performed well in all categories, it was also one of the larger instruments, it was the most expensive instrument evaluated, and it was equipped with features that may be superfluous. Performance in accuracy and reproducibility may, in many instances, be improved with user training and the addition of compounds of interest to user libraries.

References

- ¹ Evaluation of Thermo Scientific FirstDefender RM™ Raman Spectrometer, January 2011, www.nfstc.org
- ² Evaluation of DeltaNu® ReporteR™ Raman Spectrometer, January 2011, www.nfstc.org.
- ³ Evaluation of ICx Fido® Verdict™ Portable Explosives and Narcotics Identifier, January 2011, www.nfstc.org.
- ⁴ Evaluation of Smiths Detection RespondeR™ RCI Raman Spectrometer, January 2011, www.nfstc.org.

The NFSTC would like to acknowledge the Manatee County Sheriff's Office and especially Michael Healy for assistance with this project.

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